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INFRARED ABSORPTION BY H<sub>2</sub>O AND N<sub>2</sub>O

Darrell E. Burch, et al

Philco-Ford Corporation

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#### ABSTRACT

The infrared absorption by samples of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O} + \text{N}_2$  has been studied in the three spectral regions,  $1630\text{-}2290\text{ cm}^{-1}$ ,  $1250\text{-}1445\text{ cm}^{-1}$  and  $430\text{-}822\text{ cm}^{-1}$ . The samples cover a wide range of paths and pressures with temperatures up to  $433\text{ K}$ . The emphasis has been on the continuum absorption in several narrow spectral intervals where most of the absorption results from lines centered more than  $1\text{ cm}^{-1}$  from the point of observation. Absorption by the distant wings of  $\text{N}_2$ -broadened lines is less relative to self-broadened  $\text{H}_2\text{O}$  lines than it is within a few  $\text{cm}^{-1}$  of the line centers. This result is consistent with results published previously for other spectral regions.

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## SECTION 1

### INTRODUCTION AND SUMMARY

Continuum absorption by  $\text{H}_2\text{O}$  plays a very important role in the infrared absorption in certain atmospheric windows. Bignell, Saiedy and Sheppard<sup>1</sup> were among the first to attempt careful quantitative measurements of the  $\text{H}_2\text{O}$  continuum and found that it could not be predicted accurately on the basis of what was known about  $\text{H}_2\text{O}$  absorption line parameters. The two main sources of error are probably lack of knowledge about the shapes of the extreme wings of the absorption lines and possible absorption by  $\text{H}_2\text{O}:\text{H}_2\text{O}$  dimers.

The results presented here represent part of a continuing laboratory study of the absorption by  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O} + \text{N}_2$  samples with special emphasis on the continuum. A few years ago we<sup>2</sup> were able to show conclusively that the  $\text{H}_2\text{O}$  continuum in the 8-12  $\mu\text{m}$  window has a much stronger dependence on the  $\text{H}_2\text{O}$  partial pressure and less dependence on the total atmospheric pressure than had been expected. The results of Bignell et al<sup>1</sup> provided evidence of a strong dependence on  $\text{H}_2\text{O}$  partial pressure, but these workers using the sun as a radiant energy source to measure the atmospheric absorption were, of course, limited in the variations in atmospheric conditions. By using sample cells that can be evacuated and operated with  $\text{H}_2\text{O}$  or mixtures of  $\text{H}_2\text{O} + \text{N}_2$  at any desired pressure up to a few atmospheres, we<sup>2,3,4,5</sup> have been able to study the effect of  $\text{H}_2\text{O}-\text{H}_2\text{O}$  collisions as well as  $\text{H}_2\text{O}-\text{N}_2$  collisions. The effects of temperature changes have also been studied.

The parameters of nearly all of the  $\text{H}_2\text{O}$  lines of significance in the infrared have been compiled and recorded on magnetic tape.<sup>6</sup> The tabulated parameters for each line are: line center  $\nu_0$ , intensity  $S$ ,



half-width  $\alpha_0$  normalized for air at 1 atm and 296K, and  $E''$ , the lower energy level involved in the transition. By knowing  $E''$ , the influence of temperature on  $S$  can be computed. The line parameters have a combined experimental-theoretical basis. Transmission spectra calculated on the basis of these parameters generally agree well with experimental results when averaged over intervals several  $\text{cm}^{-1}$  wide in regions where most of the absorption arises from lines centered within 20 or 30  $\text{cm}^{-1}$ . However, as pointed out above, the continuum absorption in the window regions cannot be calculated accurately on the basis of the line parameters. Long et al<sup>7</sup> have used a CO laser as a radiant energy source to measure the transmittance of synthetic atmospheres of  $\text{H}_2\text{O} + \text{N}_2$  in a few narrow windows separated by a few  $\text{cm}^{-1}$  from any  $\text{H}_2\text{O}$  lines of significance. These windows occur in a region containing many  $\text{H}_2\text{O}$  lines of medium intensity between approximately 1840 and 1990  $\text{cm}^{-1}$ . In nearly every case, the absorptance observed by Long et al was greater than that calculated on the basis of the tabulated line parameters and the Lorentz line shape. In some cases the discrepancy was as large as a factor of 3. Rice<sup>8</sup> has also found that the calculated absorption does not agree well with his experimental results obtained by using a CO laser as an energy source in a manner different from that used by Long et al.

In a previous report,<sup>3</sup> we presented results of measurements made in more than 40 narrow windows between 1630 and 2300  $\text{cm}^{-1}$ , including several of those studied by Long et al. Where comparisons could be made, the experimental results of the two studies agree quite well. The previous study<sup>3</sup> included pure  $\text{H}_2\text{O}$  samples as well as samples of  $\text{H}_2\text{O} + \text{N}_2$  at different temperatures. The results indicate the wings of both self-broadened and  $\text{N}_2$ -broadened lines more than a few  $\text{cm}^{-1}$  from the centers absorb more than Lorentz lines having the same intensities and widths. The shapes of the self-broadened lines are also quite different from those of  $\text{N}_2$ -broadened lines.

An  $\text{H}_2\text{O}:\text{H}_2\text{O}$  dimer has been suggested as the source of much of the  $\text{H}_2\text{O}$  continuum absorption between 8 and 12  $\mu\text{m}$ . It seems unlikely that dimers can account for the extra absorption observed in the narrow windows between 1840 and 1990  $\text{cm}^{-1}$  by us and by Long et al. Lack of knowledge about the shapes of the wings of lines probably accounts for the inability to calculate the absorption in the narrow windows between 1630 and 2300  $\text{cm}^{-1}$ . The wings of very strong, distant lines may also account for much of the continuum absorption in the 8-12  $\mu\text{m}$  window. It is difficult to distinguish between dimer absorption and absorption by the extreme wings of lines since both types display the same type of dependence on pressure and path length.

The data presented in Sections 2, 3, and 4 are from a similar study in the 1230-1450  $\text{cm}^{-1}$  and 430-822  $\text{cm}^{-1}$  regions. Sections 2 and 3 contain transmittance curves and tables that can be used to check the

tabulated line parameters. Data on the continuum absorption in several narrow windows in these spectral regions are summarized and tabulated in Section 4. We expect to obtain in the near future similar data in the same spectral regions with samples near room temperature. Comparisons of the experimental data with calculated results are expected to provide new insight into mechanisms of dimer absorption and the shapes of the extreme wings of lines.

Section 5 contains a brief summary of work on the compilation of the parameters of  $N_2O$  lines. Most of the results have been given in detail previously.<sup>9</sup> These data, along with a few minor modifications and additions that have been made, are available in Reference 6.

#### Symbols, Units, and Definitions

At the pressures involved in the present study, the  $H_2O$  vapor density is proportional to its partial pressure  $p$  so that the absorber thickness  $u$  of a sample is given by

$$\begin{aligned} u(\text{molecules/cm}^2) &= 2.69 \times 10^{19} p(\text{atm}) L(\text{cm}) (273/\theta) \\ &= 7.34 \times 10^{21} pL/\theta. \end{aligned} \quad (1-1)$$

The true transmittance that would be observed with infinite resolving power is given by

$$T' = \exp(-u\kappa), \quad \text{or} \quad (-1/u) \ln T' = \kappa, \quad (1-2)$$

where  $\kappa$  is the absorption coefficient. Because of the finite slitwidth of a spectrometer and possible variations in  $\kappa$  with wavenumber due to line structure, the observed transmittance  $T$  may differ from  $T'$  at the same wavenumber. The quantity  $T$  represents a weighted average of  $T'$  over the interval passed by the spectrometer.

The intrinsic absorption coefficient due to a single collision-broadened absorption line at a point within a few  $\text{cm}^{-1}$  of the line center,  $\nu_0$ , is probably given adequately by the Lorentz shape:

$$k = \frac{S}{\pi} \frac{\alpha}{(\nu - \nu_0)^2 + \alpha^2}. \quad (1-3)$$

The line intensity  $S = \int k d\nu$  is essentially independent of pressure for the conditions of the present study. It has been shown<sup>9,10,11</sup> that for  $|\nu - \nu_0|$  greater than a few  $\text{cm}^{-1}$ , the Lorentz equation may require modification. One method is to employ a factor  $X$ , which is a function of  $(\nu - \nu_0)$ , so that Eq. (1-3) becomes

$$k = k_L \chi = \frac{S}{\pi} \frac{\alpha \chi}{(\nu - \nu_0)^2 + \alpha^2}, \quad (1-4)$$

where  $k_L$  denotes the value given by the Lorentz coefficient. The value of  $\chi$  is approximately equal to unity for small  $|\nu - \nu_0|$ , but may be quite different for large  $|\nu - \nu_0|$ . For example,  $\chi \ll 1$  for the extreme wings of  $\text{CO}_2$  lines, but the data presented below indicates  $\chi > 1$  for  $\text{H}_2\text{O}$  lines.

The half-width  $\alpha$  is proportional to pressure so that  $k$  is, in turn, proportional to pressure in the extreme wings where  $|\nu - \nu_0| \gg \alpha$ . It follows from Eq. (1-4) that the wing-absorption coefficient  $C$  due to the extreme wings of several lines is equal to the sum of all the  $k$ 's due to the individual lines and is proportional to pressure, ( $C = C^0 p$ ). Since wing absorption changes slowly with wavenumber, it is frequently called continuum absorption.

Continuum absorption may also arise from dimers,<sup>12</sup> such as  $\text{H}_2\text{O}:\text{H}_2\text{O}$ , or from pressure-induced bands. These two types of continuum have the same pressure dependence as absorption by line wings; therefore, it is not necessary to determine which is the source of the absorption being measured. In the following discussions, we refer to it as wing absorption, although it is possible that some dimer absorption or pressure-induced absorption also occurs. The absorption coefficient due to local lines whose centers occur within a few  $\text{cm}^{-1}$  of the point of observation is denoted by  $\kappa(\text{local})$ . This quantity may vary rapidly with wavenumber and depends on pressure as indicated by Eq. (1-3) because of collision-broadening of the absorption lines. At a given wavenumber, there may be absorption by local lines as well as by continuum. Therefore, for a pure  $\text{H}_2\text{O}$  sample, the total absorption coefficient  $\kappa$  in Eq. (1-2) is given by

$$\kappa = \kappa(\text{local}) + C_s^0 p. \quad (1-5)$$

The normalized continuum coefficient  $C_s^0$  is the value of  $C_s$  when  $p = 1$  atm. The subscript  $s$  denotes self-broadening of the lines. Since  $u$  is proportional to  $pL$ , ( $- \ln T$ ) due to continuum is proportional to  $p^2 L$ .

For a mixture of  $\text{H}_2\text{O} + \text{N}_2$ , such as several of those used in the present study, Eq. (1-5) must be modified to account for the broadening of the  $\text{H}_2\text{O}$  lines by  $\text{N}_2$ .

$$\kappa = \kappa(\text{local}) + C_s^0 p + C_{\text{N}_2}^0 p_{\text{N}_2}, \quad (1-6)$$

where  $p_{\text{N}_2}$  is the partial pressure of  $\text{N}_2$ .

The equivalent pressure  $P_e$  given by the following equation is a convenient parameter when dealing with  $H_2O$  absorption by mixtures of  $H_2O$  in  $N_2$  or in air, which is approximately 80%  $N_2$ :

$$P_e = Bp + p_{N_2} = (B-1)p + P, \quad (1-7)$$

where  $P$  is the total pressure.  $B$  is the ratio of the self-broadening ability to the broadening ability of  $N_2$ , i.e.,  $C_s^O/C_{N_2}^O$ . We note that  $P_e$  approximates  $P$  for dilute mixtures of  $H_2O$  in  $N_2$  ( $p \ll p_{N_2}$ ).

### Experimental Procedures

The data presented in Sections 2, 3, and 4 were obtained from samples contained in a multiple-pass absorption cell with 1-meter base length. The cell can be heated to temperatures as high as 475 K and can be evacuated or pressurized to more than 20 atmospheres. Spectral curves were scanned with a custom-made grating monochromator employing a liquid-helium cooled Ge:Cu detector. All of the optical path outside of the sample cell is contained in a vacuum tank to eliminate absorption by atmospheric gases. This is particularly important when studying the strong  $H_2O$  bands. A paper<sup>13</sup> published previously describes the apparatus and the experimental procedures.

In a previous report<sup>4</sup> dealing with continuum absorption, we have discussed some unexplained absorption that occurred in certain spectral regions. The absorption bands were quite broad with little or no spectral structure and appeared to result from an impurity in the samples. At some wavelengths, some of the absorption appeared to result from a film of impurity on the mirror surfaces. In other cases, the absorption was apparently due to a gaseous impurity in the sample. During the present experiment, we observed an impurity band between approximately 650 and 1100  $cm^{-1}$  that seriously decreased the accuracy of the  $H_2O$  data obtained in this region. After some extensive testing, we determined that this impurity band resulted from vapor that "out-gassed" from the silicone O-ring gaskets in the sample cell. If the cell were left evacuated but with the valve to the vacuum pump closed, absorption by this band increased and was quite strong, even when the pressure was much less than one torr. Some impurity remained when the valve was opened to the mechanical vacuum pump; however, the impurity could be flushed out by adding  $N_2$ , or some other gas, and evacuating the cell. After the cell was properly "cleaned" several minutes were required for the absorption to become significant. Quick tests made on the vapor from a variety of heated silicone and buna-N gasket materials showed that all have an absorption band in this spectral region, although not all of the bands are alike. The gaskets from which vapor was first observed had been in the cell for several months and had been heated to approximately 425 K for a few days. The outgassing apparently continues almost indefinitely.

Because of the time required for a significant amount of the impurity to accumulate after the cell had been flushed, it was possible to obtain data on the absorption by a pure  $\text{H}_2\text{O}$  sample at a fixed wavenumber. However, it was not practical to scan spectral curves in the  $650\text{-}823\text{ cm}^{-1}$  region because of the accumulation of the impurity during the time required to scan the spectrum. It was also not possible to obtain reliable data on  $\text{H}_2\text{O} + \text{N}_2$  samples because of the time required to mix the sample and make the measurements. Consequently, results on the continuum absorption at a few points between  $650$  and  $822\text{ cm}^{-1}$  are given in Section 4 for pure  $\text{H}_2\text{O}$ , but no spectral curves are presented, nor are any continuum data on  $\text{H}_2\text{O} + \text{N}_2$  mixtures.

## SECTION 2

### SPECTRAL TRANSMITTANCE FROM 1250 TO 1445 $\text{cm}^{-1}$

Figures 2-1 and 2-2 show spectral curves of transmittance for 2 samples of pure  $\text{H}_2\text{O}$  at 391 K. Figures 2-3 and 2-4 show similar curves for 3 samples at a higher temperature, 433 K. The samples represented cover wide ranges of pressure and absorber thickness. The parameters of many of the  $\text{H}_2\text{O}$  absorption lines in this spectral region listed in Reference 6 can be checked by comparing the experimental curves in Figs. 2-1 through 2-4 with calculated curves based on the listed parameters. Table 2-1 contains several values of the integrated absorptance for the samples represented in the figures. The integrated absorptance between any 2 of the wavenumbers listed can be found by taking the difference between the two corresponding values of the cumulative integrated absorptance listed in the table. No absorption by impurities was observed in this spectral region.

Seven narrow spectral intervals that are relatively free of absorption lines have been studied in more detail in order to measure the continuum absorption. The results are given in Section 4.



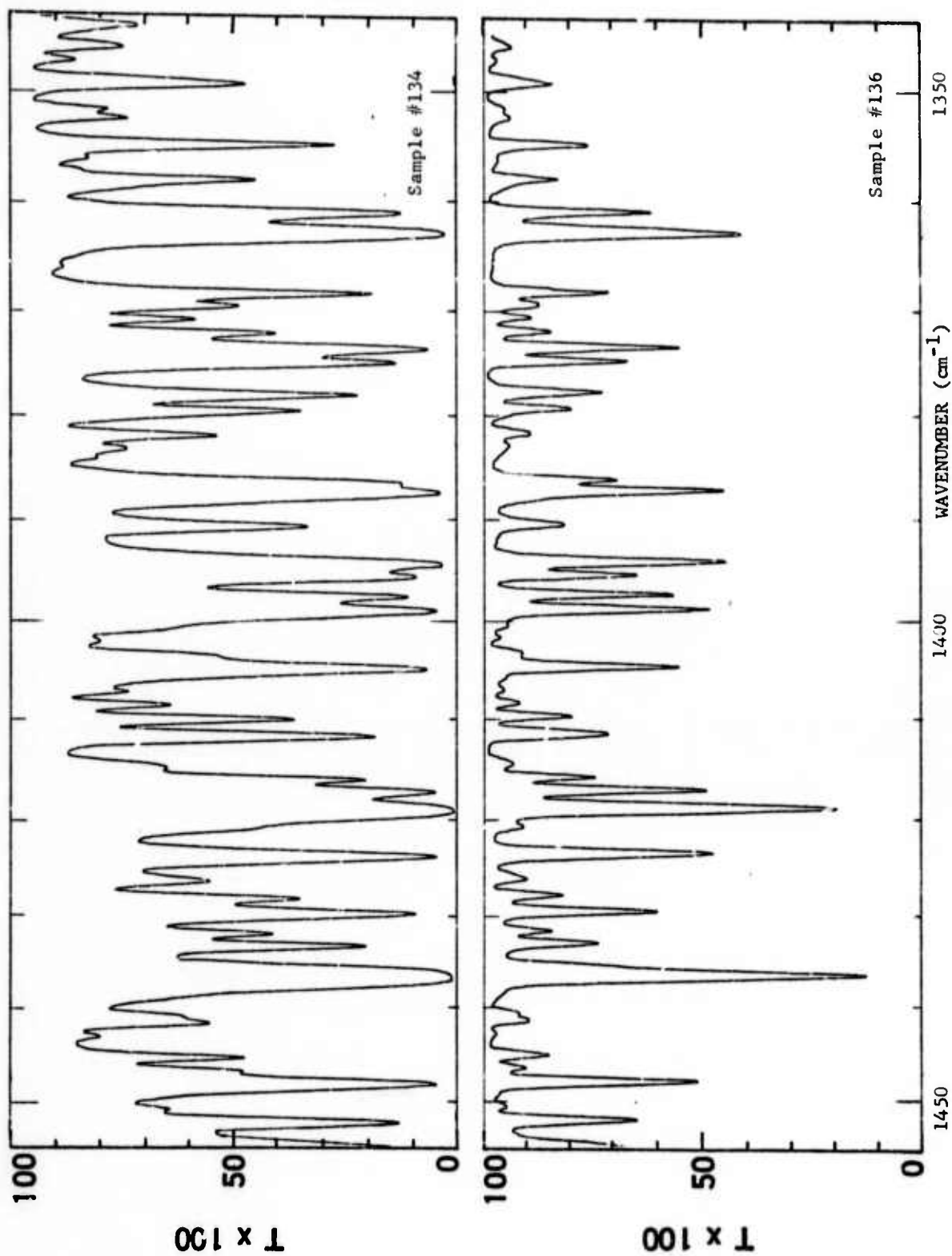


FIG. 2-1. Spectral transmittance curves of pure  $H_2O$  between  $1345\text{ cm}^{-1}$  and  $1455\text{ cm}^{-1}$ . Spectral slitwidth  $\approx 0.7\text{ cm}^{-1}$ .

Sample	temp (K)	P (atm)	u (molecules $\text{cm}^{-2}$ )
134	391	0.0842	$6.58 \times 10^{20}$
136	391	0.0184	$1.44 \times 10^{20}$

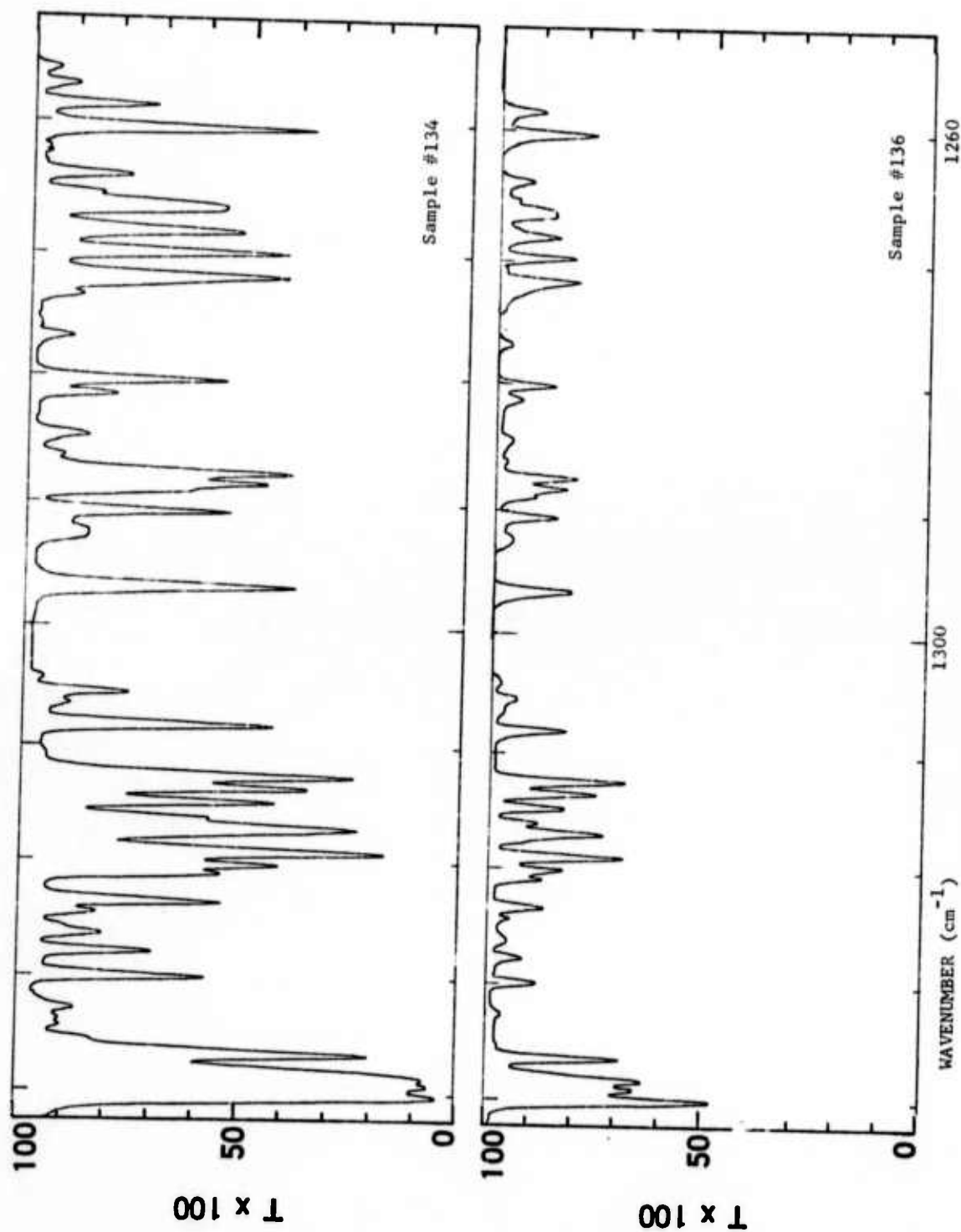


FIG. 2-2. Spectral transmittance curves of pure  $H_2O$  between  $1250\text{ cm}^{-1}$  and  $1345\text{ cm}^{-1}$ . Spectral slitwidth  $\approx 0.6\text{ cm}^{-1}$ .

Sample	temp (K)	P (atm)	$\nu$ (molecules $\text{cm}^{-2}$ )
134	391	0.0842	$6.58 \times 10^{20}$
136	391	0.0184	$1.44 \times 10^{20}$



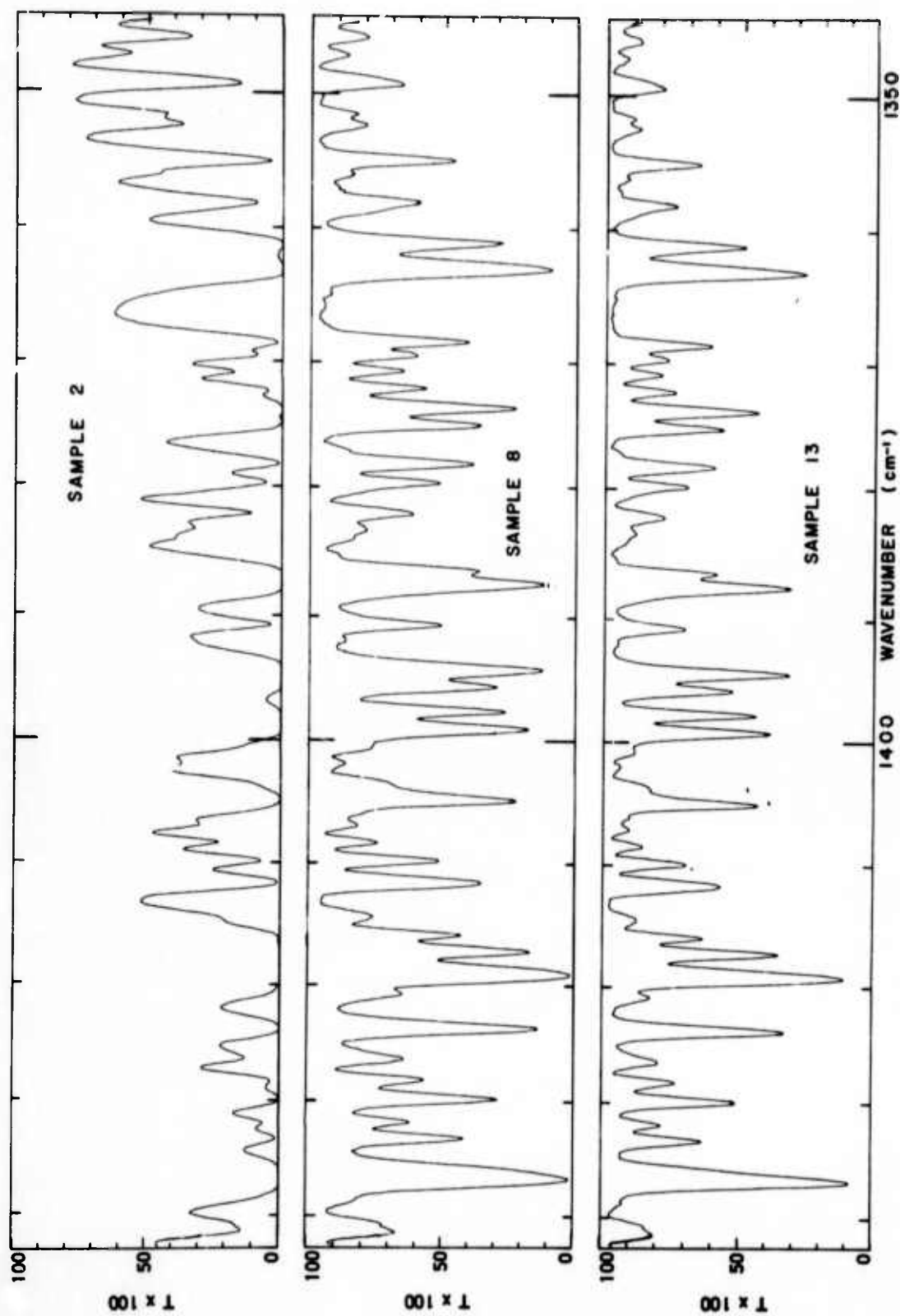


FIG. 2-3. Spectral curves of transmittance from 1440 to 1345  $\text{cm}^{-1}$  for 3 pure  $\text{H}_2\text{O}$  samples. Spectral slitwidth  $\approx 0.6 \text{ cm}^{-1}$ .

Sample	P (atm)	$\theta$ (K)	u (molecules $\text{cm}^{-2}$ )
2	0.2	433	14.1 E20
8	0.02	433	8.39 E20
13	0.02	433	2.80 E20

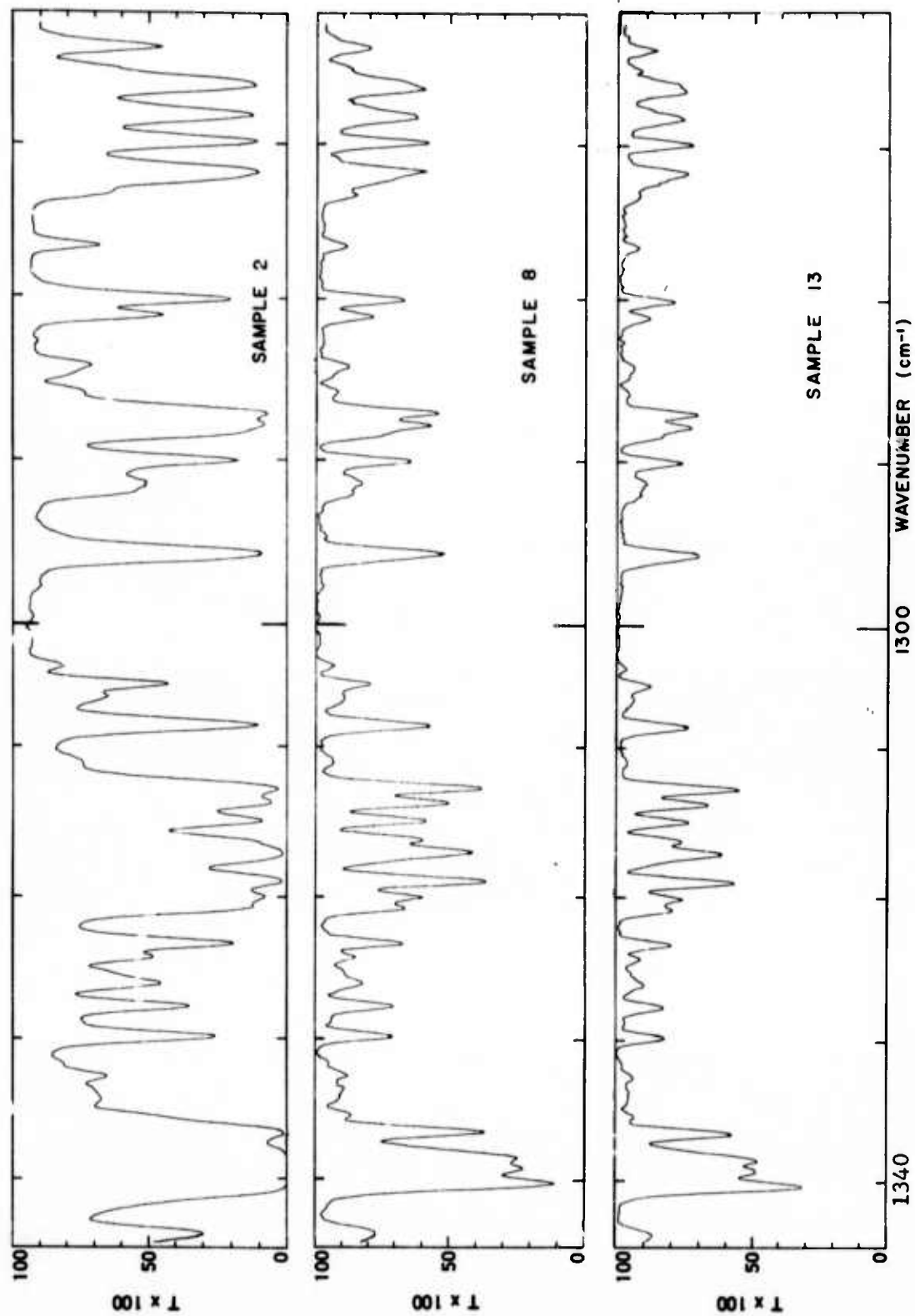


FIG. 2-4. Spectral curves of transmittance from 1345 to 1260  $\text{cm}^{-1}$  for 3 pure  $\text{H}_2\text{O}$  samples. Spectral slitwidth  $\approx 0.7 \text{ cm}^{-1}$ . Sample parameters are listed in Fig. 2-3.

TABLE 2-1

INTEGRATED ABSORPTANCE FOR H<sub>2</sub>O

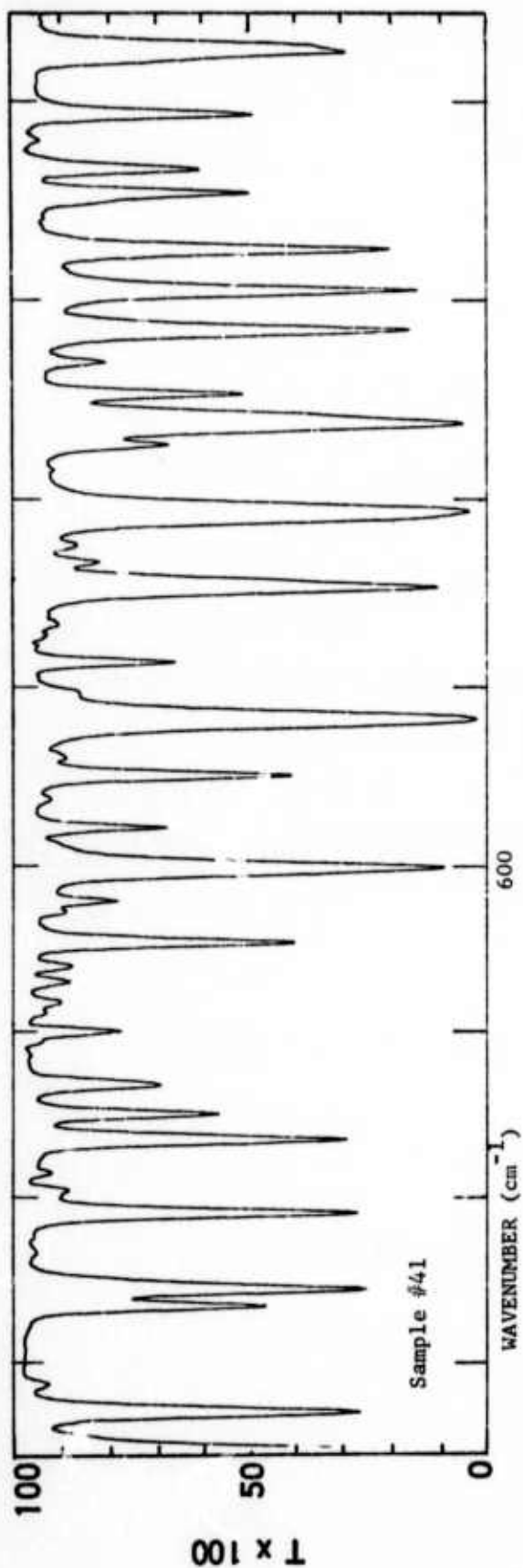
$$\int_{\nu'}^{\nu} (1-T) d\nu (\text{cm}^{-1})$$

Sample #	2	8	13	134	136
$\theta$ (K)	433	433	433	391	391
p (atm)	0.2	0.02	0.02	0.0842	0.0184
u (molecules <sup>-1</sup> cm <sup>2</sup> )	14.1 E20	8.39 E20	2.80 E20	6.58 E20	1.44 E20
$\nu$ (cm <sup>-1</sup> )	$\nu'$ (cm <sup>-1</sup> ) = 1262	1262	1262	1252	1252
1260				0.377	0.097
1265	0.708	0.257	0.146	1.055	0.332
1270	3.810	1.437	0.846	2.410	0.693
1275	6.080	2.218	1.320	3.393	0.970
1280	6.894	2.473	1.473	3.653	1.025
1285	8.215	2.918	1.716	4.155	1.194
1290	10.859	3.810	2.249	5.360	1.525
1295	12.664	4.378	2.606	5.995	1.689
1300	14.218	4.911	2.948	6.671	1.860
1305	14.660	4.995	2.988	6.794	1.885
1310	16.728	5.647	3.368	7.617	2.109
1315	19.930	6.889	4.166	9.293	2.619
1320	24.191	8.602	5.189	11.665	3.243
1325	27.005	9.450	5.677	12.905	3.567
1330	29.117	10.137	6.058	13.638	3.767
1335	30.531	10.510	6.249	14.122	3.894
1340	34.953	12.929	7.765	17.249	4.847
1345	38.058	14.161	8.597	18.798	5.371
1350	40.527	14.894	9.060	19.851	5.631
1355	42.831	15.562	9.429	20.794	5.864
1360	46.023	16.539	10.009	22.142	6.175
1365	50.570	18.787	11.502	25.280	7.234
1370	53.730	19.765	12.049	26.789	7.599
1375	58.140	21.654	13.173	29.483	8.295
1380	62.304	23.160	14.099	31.799	8.864
1385	65.572	24.086	14.620	33.092	9.124
1390	69.942	26.098	15.874	35.927	9.981
1395	74.228	27.904	16.938	38.496	10.723
1400	79.164	30.521	18.599	42.385	11.890
1405	83.149	31.867	19.321	44.424	12.303
1410	86.924	33.053	20.035	46.248	12.745
1415	90.657	34.355	20.843	48.159	13.218
1420	95.528	37.466	23.044	52.136	14.830
1425	100.146	39.345	24.176	55.095	15.592
1430	104.484	40.858	25.035	57.460	16.100
1435	109.093	42.508	25.979	60.208	16.757
1440	113.695	44.858	27.613	63.559	18.105
1443	115.843	45.463	27.953	64.474	18.279

### SECTION 3

#### SPECTRAL TRANSMITTANCE FROM 430 TO 634 $\text{cm}^{-1}$

Figures 3-1 and 3-2 show spectral transmittance curves for 3 samples of pure  $\text{H}_2\text{O}$ . Values of integrated absorptance for the same samples are listed in Table 3-1. The continuum absorption coefficient has been measured at several points within this interval and at a few points between 634 and 822  $\text{cm}^{-1}$ . Results of the continuum measurements are given in Section 4. No spectral transmittance curves are shown between 634 and 822  $\text{cm}^{-1}$  because of the problems with impurities discussed in Section 1.



3-2

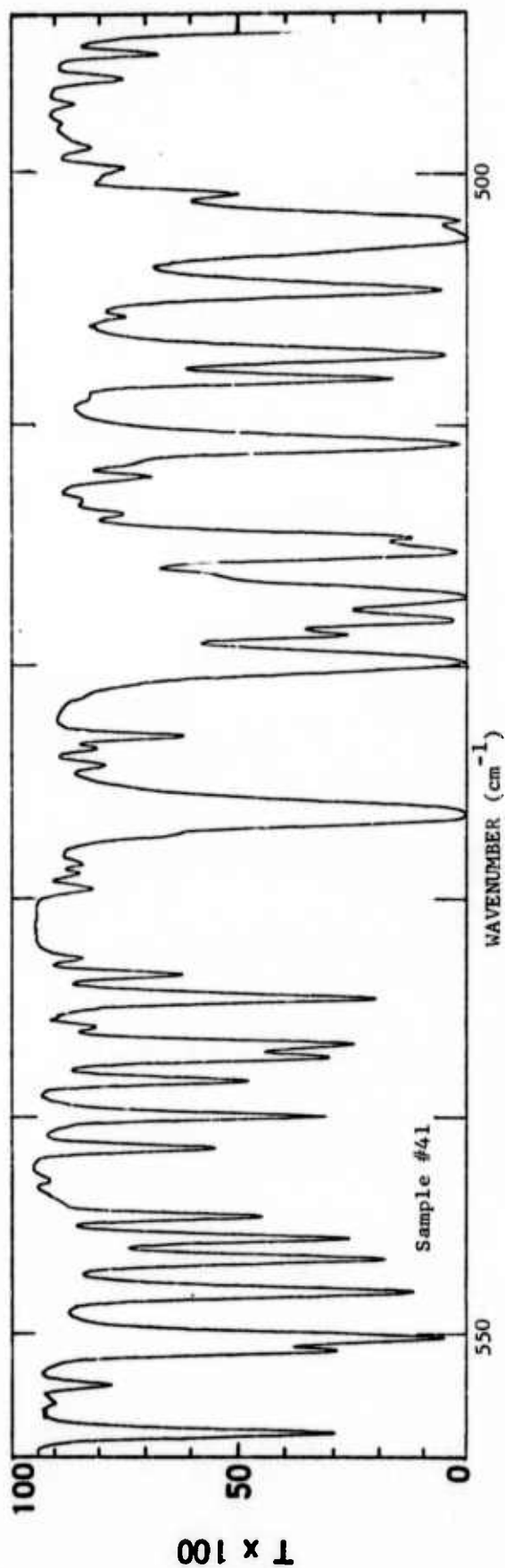


FIG. 3-1. Spectral transmittance curve of pure  $\text{H}_2\text{O}$  between 495  $\text{cm}^{-1}$  and 634  $\text{cm}^{-1}$ . Spectral slitwidth  $\approx 0.4 \text{ cm}^{-1}$ . Sample parameters are  $\theta = 428^\circ\text{K}$ ,  $p = 0.1 \text{ atm}$ , and  $u = 7.14 \times 10^{20} \text{ molecules cm}^{-2}$ .

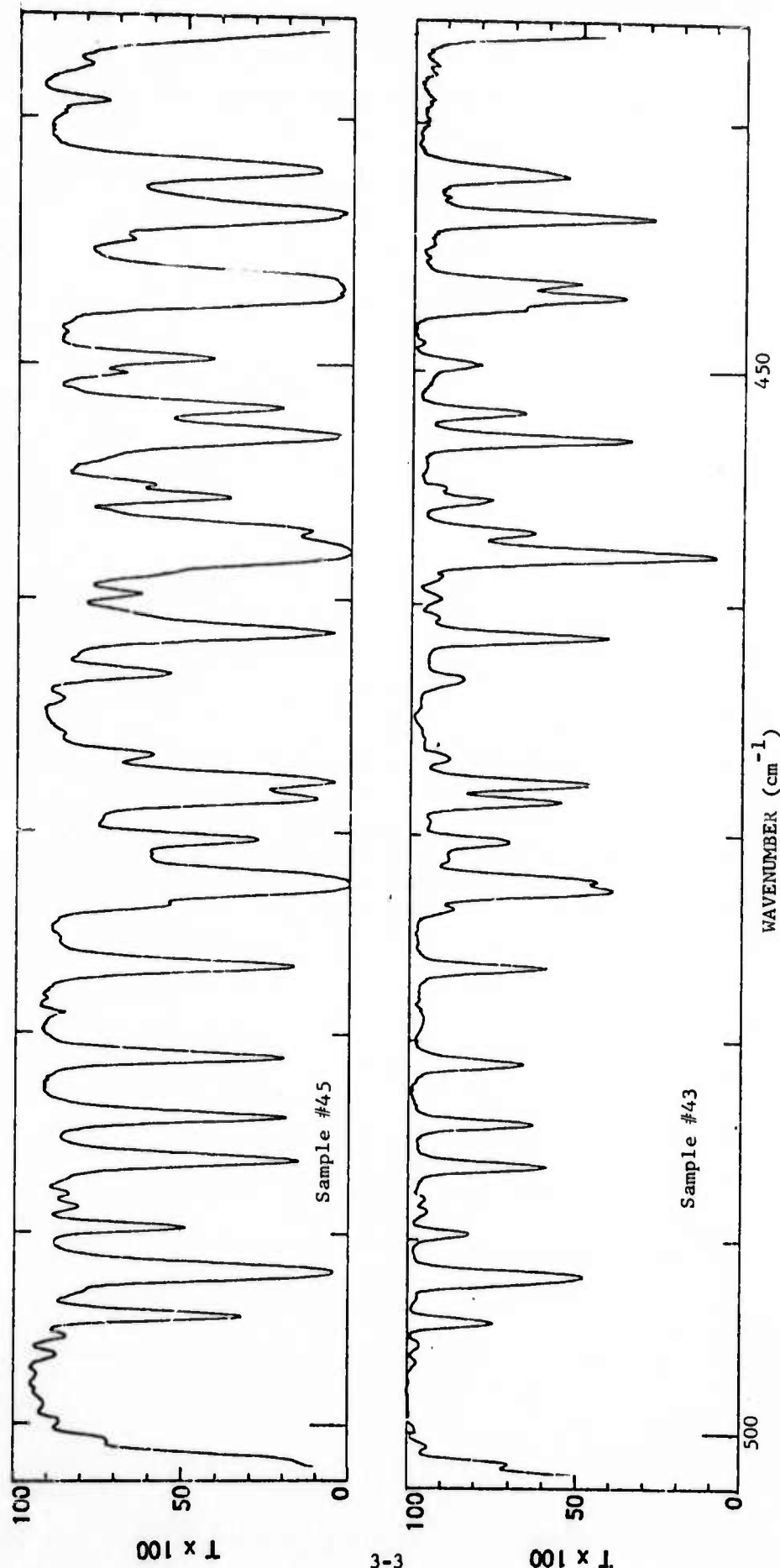


FIG. 3-2. Spectral transmittance curves of pure  $\text{H}_2\text{O}$  between  $437\text{ cm}^{-1}$  and  $502\text{ cm}^{-1}$ . Spectral slitwidth  $\approx 0.6\text{ cm}^{-1}$ .

Sample	temp (K)	P (atm)	u (molecules $\text{cm}^{-2}$ )
43	425	0.0198	$1.42 \times 10^{20}$
45	425	0.0684	$4.92 \times 10^{20}$

TABLE 3-1

INTEGRATED ABSORPTANCE FOR H<sub>2</sub>O

$$\int_{\nu}^{\nu'} (1-T) d\nu (\text{cm}^{-1})$$

Sample #	43	45	41
$\theta$ (K)	425	425	428
p (atm)	0.0198	0.0198	0.1
u (molecules <sup>-1</sup> cm <sup>2</sup> )	1.42 E20	4.92 E20	7.14 E20

$\nu$ (cm <sup>-1</sup> )	$\nu'$ (cm <sup>-1</sup> )=439	439	$\nu$ (cm <sup>-1</sup> )	$\nu'$ (cm <sup>-1</sup> )=496
439	0	0	496	0
440	0.042	0.175	500	0.568
445	0.920	2.566	505	3.629
450	1.770	4.914	510	5.484
455	2.459	7.053	515	7.664
460	3.611	9.934	520	11.321
465	4.201	11.639	525	12.356
470	4.943	13.734	530	14.196
475	5.975	16.274	535	15.131
480	6.341	17.356	540	16.727
485	6.852	18.885	545	17.535
490	7.323	20.342	550	19.621
495	7.978	22.243	555	21.021
500	8.053	22.695	560	21.959
			565	22.861
			570	24.215
			575	25.397
			580	26.877
			585	28.935
			590	29.538
			595	31.139
			600	32.012
			605	33.242
			610	33.647
			615	34.265
			620	35.065
			625	35.920
			630	36.835
			634	37.565



## SECTION 4

### CONTINUUM ABSORPTION

The objective of this portion of the investigation was to determine the values of the continuum absorption coefficients  $C_s^0$  and  $C_{N_2}^0$  for  $H_2O$  at points of maximum transmittance within narrow windows. The  $N_2$  results are listed in Table 4-1. Similar results for the 1630-2290  $cm^{-1}$  region have been reported previously<sup>3</sup> and have been repeated in Table 4-2 for easy reference. It is apparent from the spectral curves shown in Sections 2 and 3 that most of the absorption at some of these points is due to lines centered within 3-5  $cm^{-1}$  at the point of observation. On the other hand, much of the absorption at some of the points probably results from more distant lines. By comparing the continuum coefficients at these points at various temperatures, and by comparing them with calculated values, we expect to provide information about  $H_2O:H_2O$  dimer absorption and about the shapes of the extreme wings of lines.

Short spectral scans were made over one or more of the narrow windows of interest. Additional  $H_2O$  or  $N_2$  was added and another scan was made; this procedure was repeated typically for 6 to 8 different pressures. At the wavenumbers chosen, there was usually very little spectral structure and no absorption lines within the spectral slitwidth of the spectrometer. However, in a few cases, it was necessary to account for the effect of the finite slitwidth in order to use the observed transmittance in place of true transmittance in Eq. (1-2). It is intended that the quantity listed in Tables 4-1 and 4-2 represent all of the absorption except for that due to lines centered within approximately 0.5  $cm^{-1}$ . The estimated uncertainty for the values of  $C_s^0$  and  $C_{N_2}^0$  vary from  $\pm 10\%$  to  $\pm 20\%$ .

In previous studies<sup>3,5</sup> we have found that  $C_s^0$  decreases rapidly with increasing temperature at wavenumbers where most of the continuum absorption results from some source other than lines centered within 20-30  $cm^{-1}$ .



The source of the absorption may be either the extreme wings of lines or dimers. Many of the wavenumbers listed in Tables 4-1 and 4-2 do not show such a definite temperature dependence. The difference in behavior can be attributed to the strong positive dependence of the intensities of the lines centered between 0.5 and approximately  $30\text{ cm}^{-1}$  from the point of observation. This strong positive dependence tends to cancel the effect of the negative temperature dependence of the dimer absorption and extreme wing absorption.

As in the previous studies  $B = C_{\text{O}}^{\text{O}}/C_{\text{N}_2}^{\text{O}}$  varies from a minimum of approximately 5 upward. At wavenumbers where most of the continuum absorption is apparently due to lines centered within approximately  $5\text{ cm}^{-1}$ , the value of 5 is appropriate for B. At points where most of the absorption is due to dimers or to the extreme wings of lines, a larger value of B is consistently observed. This implies that near the line center, self-broadened lines have approximately the same shape and width as  $\text{N}_2$ -broadened lines at 5 times the pressure. However, in the extreme wings of the lines, the relative absorption by the self-broadened lines may be much greater. The results of Bignell and of Palmer are consistent with this conclusion.

TABLE 4-1

H<sub>2</sub>O CONTINUUM COEFFICIENT FOR SELF-BROADENING AND N<sub>2</sub>-BROADENING

$\nu$ (cm <sup>-1</sup> )	Multiply all values by 10 <sup>-24</sup> molecules <sup>-1</sup> cm <sup>2</sup> atm <sup>-1</sup>						B = C <sub>s</sub> <sup>o</sup> /C <sub>N</sub> <sup>o</sup>		
	C <sub>s</sub> <sup>o</sup>			C <sub>N<sub>2</sub></sub> <sup>o</sup>					
	430K	390K	350K	430K	390K	350K	430K	390K	350K
430.0	2400			349			6.9		
433.7	4520			645			7.0		
440.1	2950			378			7.8		
448.8	3420			432			7.9		
465.4	2320			296			7.8		
475.1	2640			349			7.6		
482.6	2320			353			6.6		
498.2	1200			110			10.9		
531.6	762			62			12.3		
559.2	573			44			13.1		
579.0	972			138			7.0		
597.0	670			65			10.3		
629.0	330			29			13.0		
656.0	219								
683.5	171								
725.5	120								
764.6	97								
790.0	87								
822.0	68								
<hr/>									
1443.5	2188	2276	2550		317	390		8.7	6.5
1413.6	2185	2066	2055		292	339		7.1	6.0
1366.9	1590	1317	1362		221	242		6.0	5.6
1331.1	460	446	378		59	50		7.6	7.6
1301.7	154	144	164		15.2	9.63		9.5	17.1
1275.5	167	133	146		19.9	12.1		6.7	12.1
1250.7		69	86.3		8.38	4.08		8.2	10.5

**TABLE 4-2**  
**H<sub>2</sub>O CONTINUUM COEFFICIENT FOR SELF-BROADENING AND N<sub>2</sub>-BROADENING**  
**(1630-2290 cm<sup>-1</sup>)**

$\nu$ cm <sup>-1</sup>	Multiply all values by 10 <sup>-24</sup> molecules <sup>-1</sup> cm <sup>2</sup> atm <sup>-1</sup>						$B = C_s^0/C_{N_2}^0$		
	$C_s^0$				$C_{N_2}^0$		428 K	353 K	308 K
	428 K	353 K	322 K	308 K	428 K	353 K	308 K	428 K	353 K
1630.5		5040		8640		871	1040		5.8
1665.5		6120		10000		1100	1360		5.6
1691.5		8410		11900		1500	1820		5.6
1725.2		4250		6770		696	723		6.1
1765.0		4570		5350		695	688		6.6
1786.5		2810		3420		419	425		6.7
1814.5		1490		1890		195	190 *		7.7
1839.8		1780		2160		283	297 *		6.3
1854.6 L	583	845			83.1	90		7.0	9.3
1882.0 L	419	560	724 *		57.0	58		7.3	9.6
1900.0	371		619 *					6.5	
1905.6	488	600	808 *		84.5	91.5		5.8	6.6
1920.5	1640		1900 *		296			5.5	
1927.1	433		654 *						
1929.2	281	342	478 *		42.9	41.0		6.6	8.4
1931.3	285	372	488 *		46.4	37.7 *		6.2	9.9
1948.2	344		514 *						
1952.6 L	199	247	284		29.7	26.3 *		6.7	9.4
1959.0	222		342 *						
1962.8	238	283	392 *			39.5 *			7.2
1974.0	118		204		16.7			7.1	
1978.5	108	144	190 *		13.7	12.5 *		7.9	11.5
1983.8 L	139		218 *						
1990.0 L	766		905 *		159			4.8	
1997.4	164		222 *		27.5			6.0	
2002.3 L	93.1		157 *						
2006.4 L	139		172 *						
2008.8 L	272		330 *						
2011.8 L	122		172 *						
2029.3	61.8	77.7	105 *			6.2 *			12.5
2036.1	80.7		110 *		12.2			6.6	
2045.3	125		137 *						
2055.5	40.4		72.5 *		5.55 *			7.3	
2056.0	39.1		74.8						
2071.1	43.1	52	70.5 *		6.65 *	4.5 *		6.5	11.5
2083.6 L	37.8	42.5	59.3 *			3.8 *			11.2
2102.4 L	20.2		35.0						
2109.6 L	22.6		47.9 *		3.0 *			7.5	
2130.7 L	18	20	37.1 *		1.9 *	1.7 *		9.5	11.8
2133.0	21.1		38.2						
2169.8	8.8		25.1 *		1.2 *			7.3	
2196.7	7.0	11.8 *	23.2 *		.86 **	0.58 **		8.1	20
2223.3 L	7.9		20						
2290.0			17.9						

Estimated errors for  $C_s^0$  and  $C_{N_2}^0$  are  $\pm 5\%$  except for values marked \* and \*\* which indicate  $\pm 10\%$  and  $\pm 20\%$ , respectively. Errors in B depend on the associated values of  $C_s^0$  and  $C_{N_2}^0$ .

(This Table appeared in Ref. 3)

## SECTION 5

### N<sub>2</sub>O ABSORPTION BAND PARAMETERS

In a previous report,<sup>16</sup> we summarized the parameters for all of the N<sub>2</sub>O bands of significance for atmospheric absorption. During the early portion of the investigation reported here, we made a few minor changes and additions to the listing of the parameters. The revisions are included in the complete listing of all important atmospheric absorption lines in Reference 6.

Lines from approximately 50 N<sub>2</sub>O band systems are included in the listing. The parameters have a combined experimental-theoretical basis and provide all of the information required to determine the positions, intensities, and half-widths of the lines. In most cases, a line is included if it is sufficiently intense to produce more than 10% absorbance at the line center in a normal atmospheric path that is tangent to the earth's surface and extends above the atmosphere in both directions. Some lines intense enough to meet this criterion are omitted if their absorption is dominated by nearby N<sub>2</sub>O lines that are much more intense.

## SECTION 6

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